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# Isotopic characterisation of atmospheric nitrous oxide fourier transform infrared spectroscopy

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# Isotopic Characterisation of Atmospheric Nitrous Oxide by Fourier Transform Infrared Spectroscopy

A thesis submitted in fulfilment of the

requirements for the award of the degree

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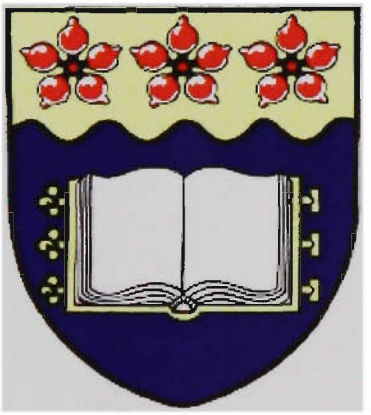
from



UNIVERSITY OF WOLLONGONG

by

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## *Certification*

I, Federico Turatti, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Department of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Federico Turatti

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***Publications***

Sections of this work described in this thesis have been reported in the following publications:

- Turatti, F., D.W.T. Griffith, S.R. Wilson, M.B. Esler, T. Rahn, H. Zhang, and G.A. Blake, Positionally dependent $^{15}N$ fractionation factors in the photolysis of $N_2O$ determined by high resolution FTIR spectroscopy, *Geophysical Research Letters*, *27* (16), 2489-2492, 2000.
- Turatti, F., D.W.T. Griffith, S.R. Wilson, M.B. Esler, L.P. Steele, T. Rahn, and H. Zhang, Isotopic analysis of atmospheric $N_2O$ by FTIR spectroscopy: $^{15}N$, $^{18}O$ and $^{15}N$ positional dependence, in *Cape Grim Baseline Air Pollution Station Annual Meeting*, edited by N. Tindale, CSIRO Atmospheric Research, Aspendale, 1999.
- Esler, M.B., D.W.T. Griffith, F. Turatti, S.R. Wilson, and T. Rahn, $N_2O$ concentration and flux measurements and complete isotope analysis using FTIR spectroscopy, *Chemosphere: Global Change Science*, *2*, 445-454, 2000.
- Griffith, D.W.T., S.R. Wilson, F. Turatti, M.B. Esler, and I.M. Jamie, Isotopomeric Analysis of Environmental Trace Gases by FTIR spectrometry: $N_2O$, $CH_4$, $CO_2$ and $H_2O$, in *1st International Symposium on Isotopomers*, edited by N. Yoshida, Yokohama, Japan, 2001.
- Wilson, S.R., D.W. Griffith, F. Turatti, and J. Menegazzo, Characterisation of agricultural $N_2O$ emission sources using isotopic labelling studies, in *Gape Grim Baseline Air Pollution Station Annual Scientific Meeting*, edited by N. Tindale, and N. Derek, Aspendale, Vic, Australia, 2000.

## *Abstract*

Nitrous oxide is the third most important anthropogenic greenhouse gas after $CO_2$ and $CH_4$ and contributes 6% of the total terrestrial radiative forcing due to greenhouse gases. It is closely involved in the depletion of stratospheric ozone by providing one of the main sources of NO radicals. Biological processes such as nitrification and denitrification are primarily responsible for $N_2O$ production. Despite its importance and years of research, the estimates of the global size of $N_2O$ sources and sinks remain highly uncertain, and its budget is not yet fully balanced.

Analysis of $N_2O$ isotopes can aid in reducing the large uncertainties in source and sink estimates by providing information that is complementary to the $N_2O$ mixing ratio. Analysis of the mean $\delta^{15}N$ and mean $\delta^{18}O$ has already lead to some insight on the $N_2O$ budget. Until very recently the intramolecular $^{15}N$ positional isotopes $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ were not measurable by any analytical technique. The intramolecular difference $\delta^{14}N^{15}N^{16}O$-$\delta^{15}N^{14}N^{16}O$ is an additional isotopic discriminator than the mean $\delta^{15}N$ alone, as it directly describes the processes forming the N-N bond in $N_2O$ production processes such as nitrification and denitrification.

This thesis describes the development of a high resolution Fourier transform infrared technique for the measurement of the $N_2O$ isotopomers $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$ and $^{14}N^{14}N^{17}O$. The FTIR technique utilises 0.012 $cm^{-1}$ resolution FTIR spectroscopy, a 2.4 m optical pathlength, 120 mL sample cell, with precise control of sample temperature and pressure. The typical analytical precision of the $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ isotopomers is of the order of 1-2 ‰, and approximately 3-4 ‰ for the oxygen isotopomers $^{14}N^{14}N^{18}O$ and $^{14}N^{14}N^{17}O$. Two independent chemometric multivariate analytical methods were developed for determination of high resolution $N_2O$ spectra: multi-micro-window classical least squares, and non-linear least squares. The strengths and limitations of the FTIR technique are analysed and compared to those of the complementary isotope ratio mass spectrometry technique. The FTIR technique is analytically robust and serves as an independent and complementary technique to $N_2O$ analysis by isotope ratio mass spectrometry.

The FTIR technique was used to analyse $N_2O$ from several contexts. The isotopic fractionation factors in the laboratory photolysis of $N_2O$ at three wavelengths were determined by analysis of the unphotolysed $N_2O$ fraction. Samples of nitrous oxide were extracted from whole air at an urban location over the period of approximately one year and isotopically characterised. The emissions of $N_2O$ from a pig effluent fertilised crop field have been isotopically characterised. In each of the three contexts, results are interpreted in relation to the processes involved.

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